

WHAT IS CLAIMED IS:

1. A UV-photoprotective oil-in-water emulsion, the oil globules of which having an average size of at most 500 nm, containing particles of at least one ionic polymer and at least one UV radiation-screening system, said screening system comprising at least one 4,4-diarylbutadiene UV-A-screening agent.
2. The oil-in-water emulsion as defined by Claim 1, devoid of surfactant.
3. The oil-in-water emulsion as defined by Claim 1, said at least one ionic polymer comprising an anionic or cationic polymer or mixture thereof, or a mixture of at least one ionic polymer and at least one nonionic polymer.
4. The oil-in-water emulsion as defined by Claim 1, said at least one ionic polymer comprising an anionic polymer.
5. The oil-in-water emulsion as defined by Claim 4, said at least one ionic polymer comprising a copolymer of isophthalic acid and/or sulfoisophthalic acid.
6. The oil-in-water emulsion as defined by Claim 5, said at least one ionic polymer comprising a copolymer of phthalate/sulfoisophthalate/glycol.
7. The oil-in-water emulsion as defined by Claim 6, said at least one ionic polymer comprising a copolymer of diethylene glycol/phthalate/isophthalate/1,4-cyclohexanedimethanol.
8. The oil-in-water emulsion as defined by Claim 5, wherein the proportion of structural units derived from sulfoisophthalic acid ranges from 2% to 20% by weight relative to the total weight of the polymer.

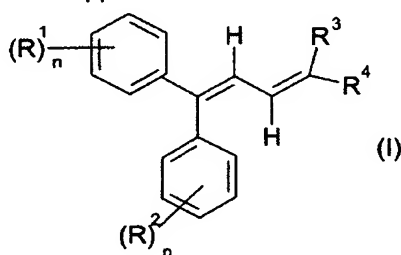
9. The oil-in-water emulsion as defined by Claim 1, comprising at least one water-dispersible ionic polymer which comprises a film-forming cosmetic vinyl copolymer.
10. The oil-in-water emulsion as defined by Claim 9, said film-forming vinyl copolymer being selected from the group consisting of:
 - (i) polyethoxylated vinyl acetate/crotonic acid copolymers;
 - (ii) vinyl acetate/crotonic acid copolymers;
 - (iii) vinyl acetate/crotonic acid/vinyl neodecanoate terpolymers;
 - (iv) N-octylacrylamide/methyl methacrylate/hydroxypropyl methacrylate/acrylic acid/tert-butylaminoethyl methacrylate copolymers;
 - (v) methyl vinyl ether/maleic anhydride alternating copolymers monoesterified with butanol; and
 - (vi) acrylic acid/ethyl acrylate/N-tert-butylacrylamide terpolymers.
11. The oil-in-water emulsion as defined by Claim 1, said at least one ionic polymer comprising a natural water-dispersible anionic polymer.
12. The oil-in-water emulsion as defined by Claim 11, said natural water-dispersible anionic polymer comprising a shellac resin, sandarac gum or dammar.
13. The oil-in-water emulsion as defined by Claim 1, comprising at least one water-dispersible ionic polymer having a weight-average molar mass ranging from 1,000 to 5,000,000.
14. The oil-in-water emulsion as defined by Claim 1, comprising particles of at least one water-dispersible ionic polymer having a particle size ranging from 10 to 400 nanometers.
15. The oil-in-water emulsion as defined by Claim 1, the particles of said at

least one ionic polymer constituting from 0.1% to 10% of the total weight of the emulsion.

16. The oil-in-water emulsion as defined by Claim 1, the weight ratio of the particles of said at least one ionic polymer to the oily phase ranging from 1/5 to 1/40.

17. The oil-in-water emulsion as defined by Claim 1, the oily phase constituting from 0.1% to 45% of the total weight of the emulsion.

18. The oil-in-water emulsion as defined by Claim 1, said at least one 4,4-diarylbutadiene UV-A-screening agent having the following formula (I):



in which the diene system is of the Z,Z; Z,E; E,Z or E,E configuration or mixture of said configurations, and wherein:

R¹ and R², which may be identical or different, are each hydrogen, a C₁-C₂₀ alkyl radical, a C₂-C₁₀ alkenyl radical, a C₁-C₁₂ alkoxy radical, a C₃-C₁₀ cycloalkyl radical, a C₃-C₁₀ cycloalkenyl radical, a C₁-C₂₀ alkoxycarbonyl radical, a C₁-C₁₂ monoalkylamino radical, a C₁-C₁₂ dialkylamino radical, an aryl radical, a heteroaryl radical or a water-solubilizing substituent selected from among a carboxylate residue, a sulfonate residue or an ammonium residue;

R³ is a group COOR⁵, COR⁵, CONR⁵R⁶, CN, O=S(-R⁵)=O, O=S(-OR⁵)=O, R⁷O-P(-OR⁸)=O, a C₁-C₂₀ alkyl radical, a C₂-C₁₀ alkenyl radical, a C₃-C₁₀ cycloalkyl radical, a C₇-C₁₀ bicycloalkyl radical, a C₃-C₁₀ cycloalkenyl radical, a

C₇-C₁₀ bicycloalkenyl radical, an optionally substituted C₆-C₁₈ aryl radical, an optionally substituted C₃-C₇ heteroaryl radical;

R⁴ is a group COOR⁶, COR⁶, CONR⁵R⁶, CN, O=S(-R⁶)=O, O=S(-OR⁶)=O, R⁷O-P(-OR⁸)=O, a C₁-C₂₀ alkyl radical, a C₂-C₁₀ alkenyl radical, a C₃-C₁₀ cycloalkyl radical, a C₇-C₁₀ bicycloalkyl radical, a C₃-C₁₀ cycloalkenyl radical, a C₇-C₁₀ bicycloalkenyl radical, an optionally substituted C₆-C₁₈ aryl radical, an optionally substituted C₃-C₇ heteroaryl radical;

the radicals R⁵ to R⁸, which may be identical or different, are each hydrogen, a C₁-C₂₀ alkyl radical, a C₂-C₁₀ alkenyl radical, a C₃-C₁₀ cycloalkyl radical, a C₇-C₁₀ bicycloalkyl radical, a C₃-C₁₀ bicycloalkenyl radical, a C₇-C₁₀ cycloalkenyl radical, an optionally substituted aryl radical, an optionally substituted heteroaryl radical;

n ranges from 1 to 3; with the proviso that the radicals R³ to R⁸ can together form, with the carbon atoms from which they depend, a C₅-C₆ ring which may be fused.

19. The oil-in-water emulsion as defined by Claim 18, wherein said compound of formula (I):

n = 1 or 2;

R¹ and R², which may be identical or different, are each hydrogen, a C₁-C₂₀ alkyl radical, a C₁-C₁₂ alkoxy radical, a C₁-C₁₂ monoalkylamino radical, a C₁-C₁₂ dialkylamino radical, a water-solubilizing substituent selected from among a carboxylate group, a sulfonate group or an ammonium residue;

R³ is a group COOR⁵, COR⁵, CONR⁵R⁶, a C₁-C₂₀ alkyl radical, a C₃-C₁₀ cycloalkyl radical, a C₃-C₁₀ cycloalkenyl radical, a C₇-C₁₀ bicycloalkyl radical, optionally substituted phenyl, naphthyl or thienyl;

R⁴ is a group COOR⁶, COR⁶, CONR⁵R⁶, a C₁-C₂₀ alkyl radical, a C₃-C₆ cycloalkyl radical, a C₃-C₁₀ cycloalkenyl radical, a C₇-C₁₀ bicycloalkyl radical, optionally substituted phenyl, naphthyl or thienyl;

the radicals R⁵ and R⁶, which may be identical or different, are each hydrogen, a C₁-C₁₂ alkyl radical, a C₃-C₁₀ cycloalkyl radical, a C₃-C₁₀ cycloalkenyl radical, a

C₇-C₁₀ bicycloalkyl radical, a C₃-C₁₀ bicycloalkenyl radical, optionally substituted phenyl or naphthyl.

20. The oil-in-water emulsion as defined by Claim 19, wherein said compound of formula (I):

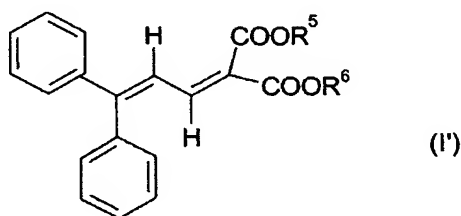
R¹ and R², which may be identical or different, are each hydrogen, a C₁-C₂₀ alkyl radical, a C₁-C₂₀ alkoxy radical, a water-solubilizing substituent selected from among a carboxylate group, a sulfonate group or an ammonium residue;

R³ is a group COOR⁵, COR⁵, CONR⁵R⁶;

R⁴ is a group COOR⁶, COR⁶, CONR⁵R⁶;

the radicals R⁵ and R⁶, which may be identical or different, are each hydrogen, a C₁-C₁₂ alkyl radical, a C₃-C₆ cycloalkyl radical, a C₃-C₁₀ cycloalkenyl radical, a C₇-C₁₀ bicycloalkyl radical, a C₃-C₁₀ bicycloalkenyl radical, optionally substituted phenyl or naphthyl.

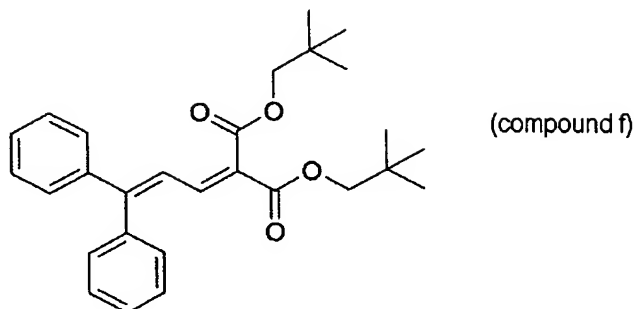
21. The oil-in-water emulsion as defined by Claim 20, said compound of formula (I) being selected from among those of the following formula (I'):



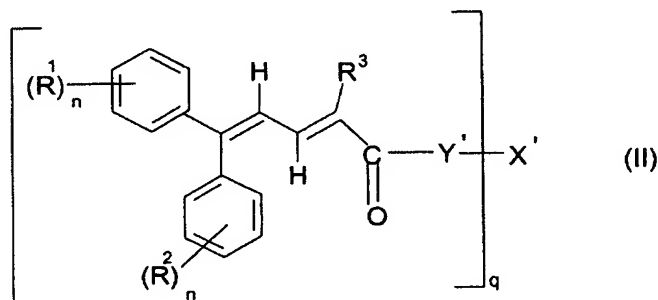
wherein the radicals R⁵ and R⁶, which may be identical or different, are each hydrogen, a C₁-C₂₀ alkyl radical, a C₃-C₆ cycloalkyl radical, a C₃-C₁₀ cycloalkenyl radical.

22. The oil-in-water emulsion as defined by Claim 21, said compound of formula (I') comprising 1,1-dicarboxy(2',2'-dimethylpropyl)-4,4-

diphenylbutadiene having the structure:



23. The oil-in-water emulsion as defined by Claim 1, said at least one 4,4-diarylbutadiene UV-A screening agent having the following formula (II):



in which the diene system is of the Z,Z; Z,E; E,Z or E,E configuration or mixture of the said configurations and wherein:

R¹, R², R³ and n have the meanings indicated in the formula (I);

Y' is a group -O- or -NR⁹-;

R⁹ is hydrogen, a linear or branched C₁-C₂₀ alkyl radical, a C₂-C₁₀ alkenyl radical, a C₃-C₁₀ cycloalkyl radical, a C₇-C₁₀ bicycloalkyl radical, a C₃-C₁₀ cycloalkenyl radical, a C₇-C₁₀ bicycloalkenyl radical, an aryl radical, a heteroaryl radical;

X' is a residue of a linear or branched, aliphatic or cycloaliphatic C₂-C₂₀ polyol comprising from 2 to 10 hydroxyl groups and having the valency q; with the proviso that the carbon chain of said residue may be interrupted by one or more sulfur or oxygen atoms, one or more imine groups, one or more C₁-C₄ alkylimino

groups; and

q ranges from 2 to 10.

24. The oil-in-water emulsion as defined by Claim 23, wherein said compound of formula (II):

R¹ and R², which may be identical or different, are each hydrogen, a C₁-C₁₂ alkyl radical, a C₁-C₈ alkoxy radical, a water-solubilizing substituent selected from among a carboxylate group, a sulfonate group or an ammonium residue;

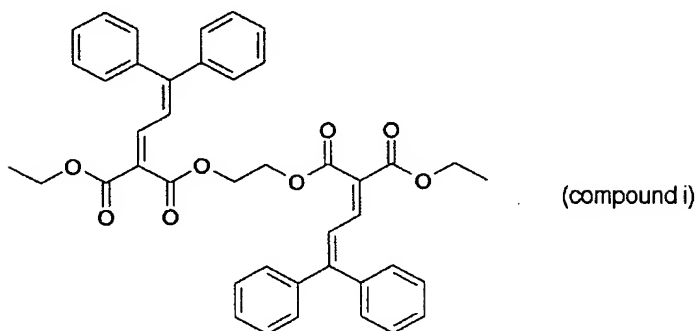
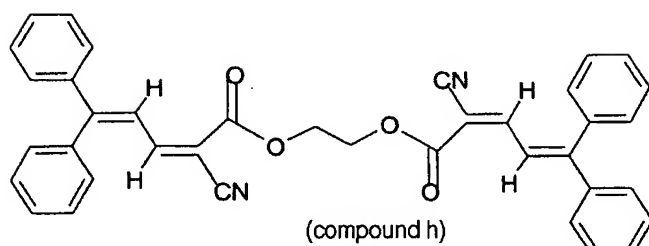
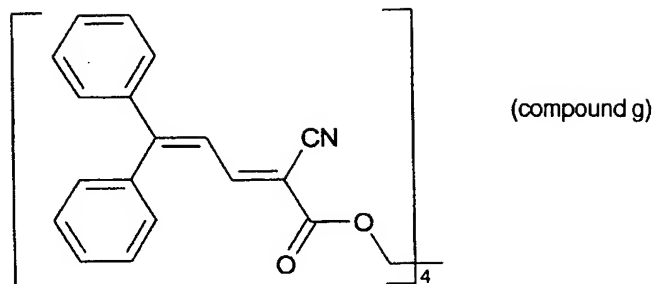
R³ is a group COOR⁵, CONR⁵R⁶, CN, a C₃-C₁₀ cycloalkyl radical, a C₇-C₁₀ bicycloalkyl radical;

R⁵ and R⁶, which may be identical or different, are each a linear or branched C₁-C₂₀ alkyl radical, a C₃-C₁₀ cycloalkyl radical, a C₇-C₁₀ bicycloalkyl radical, optionally substituted naphthyl or phenyl; and

X' is a C₂-C₂₀ polyol residue comprising from 2 to 6 hydroxyl groups.

25. The oil-in-water emulsion as defined by Claim 24, wherein said compound of formula (II), X' is an ethanol or pentaerythritol residue.

26. The oil-in-water emulsion as defined by Claim 25, said at least one compound of formula (II) being selected from among the following compounds:



27. The oil-in-water emulsion as defined by Claim 1, said at least one 4,4-diarylbutadiene UV-A screening agent constituting from 0.1% to 20% by weight relative to the total weight of the emulsion.
28. The oil-in-water emulsion as defined by Claim 1, further comprising at least one additional organic or inorganic sunscreens agent active in the UV-A and/or UV-B regions, water-soluble, fat-soluble or insoluble in the usual cosmetic solvents.
29. The oil-in-water emulsion as defined by Claim 28, comprising at least one additional organic screening agent selected from among the anthranilates; cinnamic derivatives; dibenzoylmethane derivatives; salicylic derivatives, camphor

derivatives; triazine derivatives; benzophenone derivatives; β,β' -diphenyl acrylate derivatives; benzotriazole derivatives; benzalmalonate derivatives; benzimidazole derivatives; imidazolines; bis-benzoazolyl derivatives; p-aminobenzoic acid (PABA) derivatives; benzoxazole derivatives; methylenebis(hydroxyphenylbenzotriazole) derivatives; screening polymers and screening silicones; dimers derived from α -alkylstyrene and mixtures thereof.

30. The oil-in-water emulsion as defined by Claim 29, said at least one additional organic screening agent comprising:

Ethylhexyl Salicylate,

Ethylhexyl Methoxycinnamate,

Octocrylene,

Butyl Methoxydibenzoylmethane,

Phenylbenzimidazole Sulfonic Acid,

Benzophenone-3,

Benzophenone-4,

Benzophenone-5,

n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate,

4-Methylbenzylidene camphor,

Terephthalylidene Dicamphor Sulfonic Acid,

Disodium Phenyl Dibenzimidazole Tetra-sulfonate,

2,4,6-Tris(4'-diisobutyl aminobenzalmalonate)-s-triazine

Anisotriazine,

Ethylhexyl triazone,

Diethylhexyl Butamido Triazone,

Methylene bis-Benzotriazolyl Tetramethylbutylphenol,

Drometrizole Trisiloxane,

Polysilicone 15,

2,4-Bis-[5-1-(dimethylpropyl)benzoxazol-2-yl-(4-phenyl)imino]-6-(2-ethylhexyl)imino-1,3,5-triazine, or

mixture thereof.

31. The oil-in-water emulsion as defined by Claim 28, comprising at least one additional inorganic screening agent selected from among pigments or nanopigments of metal oxides, coated or uncoated.

32. The oil-in-water emulsion as defined by Claim 31, said at least one additional inorganic screening agent comprising nanopigments of titanium oxide, amorphous or crystallized, in rutile and/or anatase form, iron oxide, zinc oxide, zirconium oxide or cerium oxide.

33. The oil-in-water emulsion as defined by Claim 1, further comprising at least one agent for artificial bronzing and/or tanning of the skin.

34. The oil-in-water emulsion as defined by Claim 1, further comprising at least one cosmetic adjuvant selected from among organic solvents, ionic or nonionic thickeners and/or gelling agents, demulcents, humectants, opacifying agents, stabilizers, emollients, silicones, insect repellents, perfumes, preservatives, surfactants, fillers, pigments, polymers, propellants, alkalinizing or acidifying agents, or any other ingredient commonly employed in the cosmetic and/or dermatological field.

35. The oil-in-water emulsion as defined by Claim 1, comprising at most 1 % by weight of an emulsifying surfactant.

36. The oil-in-water emulsion as defined by Claim 1, further comprising at least one gelling agent.

37. The oil-in-water emulsion as defined by Claim 36, said at least one gelling agent constituting from 0.1 % to 10% of the total weight of the emulsion.

38. The oil-in-water emulsion as defined by Claim 36, said at least one gelling agent comprising a water-soluble or water-dispersible nonionic or anionic associative polymer containing at least one hydrophobic sequence and at least one hydrophilic sequence.

39. The oil-in-water emulsion as defined by Claim 36, comprising at least one nonionic associative polymer selected from among:

- (1) celluloses modified with groups containing at least one hydrophobic chain;
- (2) hydroxypropylguars modified with groups containing at least one C₁₀-C₃₀ fatty chain;
- (3) polyether urethanes containing, in their chain, both hydrophilic sequences and hydrophobic sequences which may be aliphatic linkages alone and/or cycloaliphatic and/or aromatic linkages;
- (4) copolymers of vinylpyrrolidone and hydrophobic monomers with a fatty chain;
- (5) copolymers of C₁-C₆ alkyl methacrylates or acrylates and amphiphilic monomers containing at least one fatty chain; and
- (6) copolymers of hydrophilic methacrylates or acrylates and hydrophobic monomers containing at least one fatty chain.

40. The oil-in-water emulsion as defined by Claim 38, comprising an anionic associative polymer selected from among copolymers of acrylic or methacrylic acid containing a hydrophilic sequence and at least one hydrophobic sequence.

41. The oil-in-water emulsion as defined by Claim 38, comprising an anionic associative polymer selected from among:

- acrylic acid/ethyl acrylate/alkyl acrylate terpolymer;
acrylates/steareth-20 methacrylate copolymer;
oxyethylenated (25 EO) (meth)acrylic acid/ethyl acrylate/beheryl methacrylate terpolymer;

oxyethylenated (20 EO) acrylic acid/monocetyl itaconate copolymer;
oxyethylenated (20 EO) acrylic acid/monostearyl itaconate copolymer;
acrylates/acrylate copolymer modified with polyoxyethylenated (25 EO) C₁₂-C₂₄
alcohols;
ethoxylated methacrylic acid/methyl acrylate/dimethyl-meta-isopropenyl benzyl
isocyanate of behenyl alcohol terpolymer.

42. The oil-in-water emulsion as defined by Claim 36, comprising at least one gelling agent selected from among water-soluble polymers devoid of a hydrophobic chain.

43. The oil-in-water emulsion as defined by Claim 42, said polymers which are water-soluble and devoid of hydrophobic chain being selected from among homopolymers and copolymers of ethylene oxide; polyvinyl alcohols; homopolymers and copolymers of vinylpyrrolidone; homopolymers and copolymers of vinylcaprolactam; homopolymers and copolymers of polyvinyl methyl ether; nonionic acrylic homopolymers and copolymers; C₁-C₂ alkyl celluloses and derivatives thereof, hydroxymethylpropylcellulose; C₁-C₃ alkylguar or C₁-C₃ hydroxyalkylguar.

44. The oil-in-water emulsion as defined by Claim 36, said at least one gelling agent being selected from among nanometric silicas, fatty alcohols, algal derivatives, natural gums, tragacanth, clays, polysaccharide gums and synthetic polymers.

45. A method of formulating an emulsion as defined by Claim 1, comprising first mixing, with stirring, the aqueous phase, the oily phase and the polymer particles and then subjecting the mixture obtained to homogenization via cavitation.

46. The method as defined by Claim 45, the homogenization being carried out at a pressure ranging from 400 to 700 bar.

47. A method for the photoprotection of the skin, lips and/or hair against the damaging effects of UV radiation, comprising topically thereon a thus effective amount of a UV-photoprotective oil-in-water emulsion, the oil globules of which having an average size of at most 500 nm, containing particles of at least one ionic polymer and at least one UV radiation-screening system, said screening system comprising at least one 4,4-diarylbutadiene UV-A-screening agent.